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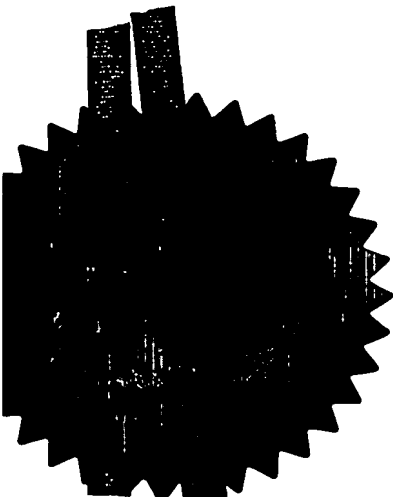
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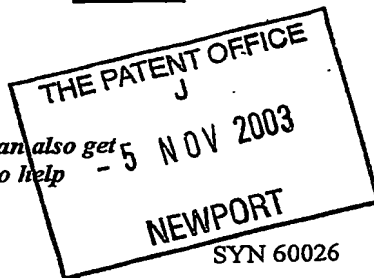
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The Patent Office

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1 Your reference

2 Patent application number
(The Patent Office will fill in this part)

0325769.8

3 Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PLC
2-4 Cockspur Street,
Trafalgar Square, London SW1Y 5BQ, UK

Patents ADP Number (if you know it)

8519803001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4 Title of the invention

Removal of mercury compounds from glycol

5 Name of Your Agent (if you have one)

GIBSON, Sara Hillary Margaret

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Johnson Matthey Catalysts
Intellectual Property Department
PO Box 1, Room N205
Belasis Avenue
Billingham
Cleveland
England, TS23 1LB

Patents ADP Number (if you know it)

8652166001

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Country	Priority Application number (if you know it)	Date of Filing (day / month / year)
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Number of earlier application	Date of Filing (day / month / year)
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Yes

Answer yes if:

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Claim(s)	1
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Translations of priority documents

Statement of Invention and right to grant of a patent (*Patents Form 7/77*)

Request for Preliminary Examination and search (*Patents Form 9/77*)

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11

I/We request the grant of a patent on the basis of this application

Signature

Date

31.10.2003

- 12 Name and daytime telephone number of person to contact in the United Kingdom

SARA HILLARY MARGARET GIBSON

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Patents Form 1/77

Removal of mercury compounds from glycol

The present invention relates to the removal of mercury compounds from mixtures of mercury and glycol compounds in particular such mixtures which are formed during a glycol drying process.

- 5 In natural gas processing plants, the gas is treated to remove acid gases, sulphur compounds and water in order to produce a gas which is suitable for distribution to the end-user. The removal of water vapour from natural gas is essential in order to avoid the formation of hydrocarbon hydrates in the gas stream and also to avoid the water condensing out of the gas in pipelines and process equipment which may then lead to
- 10 corrosion problems. For this reason the maximum amount of water allowable in processed natural gas is restricted. Several methods of removing water to depress the dew point of natural gas are practised commercially in gas-processing plants. The methods employed include contacting the gas with a bed of a solid desiccant such as a silica gel or molecular sieve, and the use of liquid desiccant compounds. In the latter case, a typical process
- 15 involves contacting the wet gas stream with a glycol solution in order to strip water from the gas stream into the glycol solution. This process is known as glycol dehydration and is very widely used in gas processing operations. The glycol solution is regenerated (i.e. dried) by removing the water in a boiler or in a flash-tank apparatus and the resulting dry glycol is recycled back to the drying process.
- 20 Mercury compounds are found in petroleum fluids such as natural gas. The concentration of mercury in natural gas is dependent on the source and may vary from very low, e.g. about 10ngm^{-3} to high e.g. $5,000\text{ngm}^{-3}$ or more. When natural gas containing mercury compounds is dried in a glycol dryer, we have found that the mercury compounds tend to partition into the glycol and thence into the water separated from the glycol during glycol
- 25 drying. The drying of the glycol for regeneration is usually done by heating at about 200°C during which process desorbed gas, water and mercury may be evolved. On cooling, the water in vented gas is condensed and discharged. This waste-water may contain significant amounts of mercury and thereby pose an environmental problem on discharge. We have developed a method of reducing the mercury discharged to the atmosphere from
- 30 NG glycol dryer equipment. According to the invention, we provide a process for removing mercury compounds from a glycol-containing stream which contains said mercury compounds comprising the step of contacting said glycol-containing stream with a bed of solid absorbent particles, said absorbent particles comprising a sulphided metal, optionally supported on support material or sulphur supported on a carbon support.

According to a further aspect of the invention, we provide a process for dehydrating a hydrocarbon stream which contains water and at least one compound of mercury or elemental mercury comprising :

a) contacting the hydrocarbon stream with a first, dry glycol stream thereby to
5 absorb at least some of the water and mercury from the hydrocarbon stream into the glycol stream, to form a second, wet, glycol stream

b) removing mercury compounds from the wet glycol stream which contains said mercury compounds by contacting said wet glycol stream with a bed of solid absorbent particles, said absorbent particles comprising a sulphided metal, optionally supported on
10 support material, or sulphur supported on a carbon support to form a third glycol stream containing a reduced concentration of mercury compared with the second glycol stream

c) drying the third glycol stream to form a fourth glycol stream which may be recirculated to step a) as a part of the first glycol stream.

The metal may be any which provides a metal compound which shows a suitable capacity
15 for being sulphided and for mercury absorption. Examples of suitable metals are iron, nickel and copper, and in particular copper and nickel, optionally a mixture of metals is used. Certain other metals, however, are generally unable to provide either compounds which can be suitably sulphided, e.g. aluminium, or sulphided compounds which can adequately absorb mercury e.g. zinc. Nevertheless, a compound of such an other metal
20 may be present as a binding or support agent which improves the structural integrity of the absorbent, and/or as a promoter which enhances the sulphiding of the precursor and/or the absorption of mercury by the absorbent. A particularly preferred other metal compound is a zinc oxide, carbonate or bicarbonate. Suitable binder materials include alumina and refractory cement compounds

25 A metal compound suitable for use in an absorbent precursor is one which may be readily sulphided and may include the oxide, carbonate, and/or basic carbonate. A particularly suitable metal compound is thus basic copper carbonate.

The absorbent comprising the metal compound in its sulphided or pre-sulphided form, may
30 be in any suitable form, e.g. as a granule, extrudate, or tablet. Particularly effective absorbents are those which are prepared from unsulphided metal compounds having a capacity to be highly sulphided. Thus, it is preferred that the amount of sulphide forming compound of the metal present in the precursor is such that the precursor may be sulphided to achieve a sulphur loading of at least 0.5% w/w, e.g. from 1 – 5% S, although
35 higher loadings of sulphur may be provided, e.g. up to about 20% w/w or greater.

The absorbent particles may comprise a pre-sulphided absorbent comprising copper and/or nickel sulphide prepared by forming a precursor comprising a copper and/or nickel compound, e.g. an extrudate comprising basic copper carbonate and a binder which is e.g. a refractory cement. Alternatively an absorbent comprising a metal sulphide formed by

5 concomitantly forming the metal sulphide during the absorption of the mercury. Since the glycol may absorb sulphur compounds such as H_2S during the drying process, it is convenient to remove the sulphur compound using a bed of a copper and/or nickel containing absorbent, thereby forming the metal sulphide in situ for removing the mercury compounds from the glycol. Where the absorbent material comprising sulphided metal

10 compounds is more difficult to handle than unsulphided absorbent, e.g. due to a weakening of the absorbent particles upon absorption of sulphur, it is preferred to use an unsulphided absorbent and form the copper and/or nickel sulphides for the removal of mercury in situ.

The sulphur compound used to sulphide the precursor may be one or more sulphur compounds such as hydrogen sulphide, carbonyl sulphide, mercaptans and polysulphides.

15 Where concomitant sulphiding and mercury absorption occurs the amount of sulphur compound that is present depends on the type of sulphur compound and metal compound used. Usually, a concentration ratio, as defined by the ratio of sulphur compound (expressed as hydrogen sulphide) concentration (v/v) to mercury concentration (v/v), of at least one, and preferably of at least 10 is used so that the precursor is sufficiently

20 sulphided. Should the initial concentration of the sulphur compound in the feed stream be below the level necessary to establish the desired ratio of sulphur compound to mercury compound concentration then it is preferred that the concentration of the sulphur compound is increased by any suitable method, e.g. by the addition of further quantities of the sulphur compound, or by the use of a molecular sieve or semi-permeable membrane to selectively

25 increase the concentration of the sulphur compound.

Alternatively, or additionally, the absorbent material may comprise sulphur supported on a carbon support.

The removal of mercury from the glycol is effected by contacting the mercury-laden liquid

30 glycol with a bed of solid absorbent particles at sufficient pressure to induce flow through the bed, normally at a pressure in the range 1 – 50 bar but optionally at greater pressure, e.g. up to about 300 bar, and at a temperature less than about 50 °C, normally at ambient temperature.

The glycols typically used in glycol drying plant include monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TREG). Triethylene glycol appears to be the most commonly used in the dehydration of natural gas.

In the process flow-sheet, the bed of absorbent is advantageously located after the glycol
5 contactor or after a flash tank (if present), the flash tank being used to remove absorbed gas from the glycol. The absorbent bed must be located so that the wet glycol contacts the absorbent before it is heated to regenerate the dry glycol.

Fig 1 shows a typical flow diagram for a glycol drying system incorporating the process of the invention. For simplicity, heat exchangers and circulation pumps have not been shown.
10 In the drawing, a wet gas stream 10 enters a glycol drying tower 12 to contact a relatively dry glycol stream 14 as the gas flows upwardly through the column. The dried gas stream leaves the column via line 16. The wet glycol stream 18 leaves the tower and passes through a mercury absorber 20 containing a bed 22 of sulphided absorbent. The glycol then passes to a glycol regeneration unit 24 and the water is removed from the glycol by heating
15 and the water and other contaminants are removed via line 26.

The experiment will be further described with reference to the following examples.

Example 1

A 3g bead of elemental mercury was contacted with 15ml of triethyleneglycol (TEG) in a 30ml glass vial. The vial and contents were mixed for 2.5 hours and then allowed to stand
20 for 20 hours. To establish the mercury level in the TEG, 2.15g of the resulting liquid mixture was diluted using mercury free acetone, to dilution factor of 6. 1.5ml of this solution was transferred to an autosampler vial and the mercury content measured using an HP6890 gas chromatograph connected to an atomic fluorescence detector. The level of elemental mercury in the TEG, after adjustment for the dilution, was found to be 2.90ppm.

25

A quantity of a commercial granular mixed oxide absorbent, PURASPEC™ 2050, available from Johnson Matthey Catalysts, was sulphided by treating at room temperature with H₂S (1%) flowing in methane at a 700 hr⁻¹ space velocity. The absorbent was taken to be fully sulphided when the H₂S in the outlet gas and inlet gas streams were substantially the same
30 and the colour of the sample had changed from green to black. The H₂S was then removed from the inlet gas and the charge was then heated to 100°C for about 2 hours in flowing methane to drive out any unreacted H₂S from the absorbent structure. The sulphided absorbent was removed and stored in an airtight container.

35 0.5ml of the sulphided absorbent was added to 5.0ml of the mercury-containing TEG in a 20ml vial, shaken vigorously, and left to stand overnight. A portion of the treated TEG was

then removed from the mixture, diluted and analysed as described previously. The mercury content was found to be below the detection limit of 2.0ppb w/v.

Example 2

- 5 The method of Example 1 was followed using TEG to which water had been added to simulate the removal of mercury from "wet" TEG as would be found in a glycol dryer effluent. The results are shown below:-

Example	TEG (ml)	Water (%)	Absorbent (g)	Hg content (ppm)	
				initial	final
1	5.0	-	0.5	2.90	<2.0
2	4.0	15.1	0.5	2.90	<2.0

Claims

1. A process for removing mercury compounds from a glycol-containing stream which contains said mercury compounds comprising the step of contacting said glycol-containing stream with a bed of solid absorbent particles, said absorbent particles comprising a
5 sulphided metal, optionally supported on support material or sulphur supported on carbon.

2. A process for dehydrating a hydrocarbon stream which contains water and at least one compound of mercury or elemental mercury comprising :

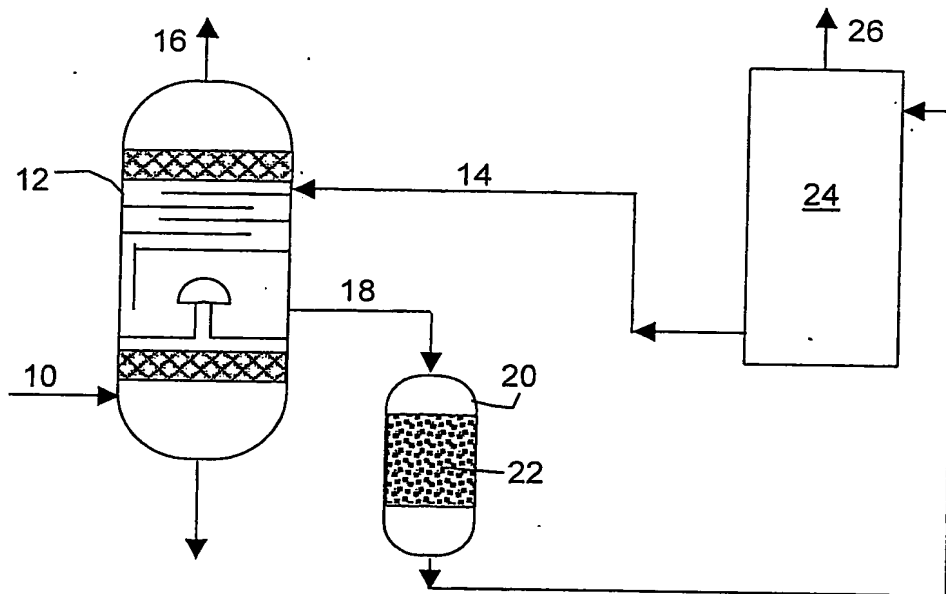
a) contacting the hydrocarbon stream with a first, dry glycol stream thereby to absorb at least some of the water and mercury from the hydrocarbon stream into the glycol
10 stream, to form a second, wet, glycol stream

b) removing mercury compounds from the wet glycol stream which contains said mercury compounds by contacting said wet glycol stream with a bed of solid absorbent particles, said absorbent particles comprising a sulphided metal,, optionally supported on support material, or sulphur supported on carbon to form a third glycol stream containing a
15 reduced concentration of mercury compared with the second glycol stream

c) drying the third glycol stream to form a fourth glycol stream which may be recirculated to step a) as a part of the first glycol stream.

Abstract

The invention is a process for removing mercury compounds from a glycol-containing stream which contains mercury compounds, especially a glycol stream which has been used in a glycol drying plant for removing water from natural gas streams. The process
5 comprises contacting the mercury-laden glycol-containing stream with a bed of solid absorbent particles, comprising a sulphided metal, optionally supported on support material or sulphur supported on carbon.

FIG 1

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